

## NEEDLELESS ELECTROSPINNING AND COATING OF POLY VINYL ALCOHOL WITH CROSS-LINKING AGENT VIA IN-SITU TECHNIQUE

MUKESH KUMAR SINHA<sup>1</sup>, BISWA RANJAN DAS<sup>2</sup>, ANURAG SRIVASTAVA<sup>3</sup> & ARVIND KUMAR SAXENA<sup>4</sup>

<sup>2,3,4</sup>Defence Materials & Stores Research & Development Establishment (Dmsrde), Kanpur, Uttar Pradesh, India

<sup>1</sup>Scientist 'D', Ff & It Division, Dmsrde, Kanpur, Uttar Pradesh, India

### ABSTRACT

Polyvinyl alcohol (PVA) crosslinked nanofibers (crosslinking agent dicarboxylic acid based) were successfully fabricated and coated on Polypropylene (PP) non woven fabric using the high speed needleless electrospinning techniques. Coating density was varied from 0.1-2.0 gms/m<sup>2</sup>. The obtained webs were characterized for surface morphology (atomic level structural), thermal, water absorbency, mechanical properties, topography (roughness) and chemical analysis. Morphological characterization revealed that on crosslinking nano fibrous web network structure converted into flattened morphological structure as compared to non crosslinked webs. Crosslinking of PVA web is occurred though esterification reactions. Topography of PVA web is severely affected by crsosslinked reactions. Fibres surface get roughened upon crosslinking the web. New crystalline morphology is developed due to crosslinking reactions as evident by DSC thermographs analysis. The morphological results were consistent and well in agreement with chemical, mechanical, absorbency and surface topography (roughness) analysis of nano fibrous web. In short, the effect of different concentrations of cross linking agent on PVA nano fibrous web, formed by high speed (throughput gms/m<sup>2</sup>) needless nanospider electrospinning process, on the web morphology and other properties is presented in this work.

**KEYWORDS:** In-Situ, Needleless Electro Spinning, Nano Fibrous Coating, Crosslinking Reactions, Polyvinyl Alcohol (PVA) Webs and Surface Morphology

### INTRODUCTION

Fibrous materials, nanofibers in particular, are considered promising support materials due to their high specific surface area <sup>1-2</sup>. Nanofibrous membranes and nanofiber composites can be produced using electrospinning <sup>3-10</sup>.

Needleless electro spinning process consists of three major components for fulfilling the process: a high voltage power supply, a spinneret electrode and collecting electrode. Such Electrospinning process utilizes a very high voltage electric field (upto 80 KVA as compared to convential se up maximum 10 KV) to produce an electrically charged jet of polymer fluid. An electrode charges the polymer fluid droplet; which ejects from spinning electrode when the repulsive forces induced by the electrostatic charge overcome the cohesive forces of surface tension and viscoelasticity of the polymer fluid. The jet splits and elongates as it accelerates under the electric field. The solvent from the fine jets evaporate rapidly due to its large surface area and it solidifies and produces a nanofibrous web which is deposited in a form of nano fibrous web on oppositely charged collecting electrode placed at a requisite distance <sup>11</sup>.

Polyvinyl alcohol has been a promising functional material due to its good chemical stability, hydrophilicity, biocompatibility and nontoxicity. Polyvinyl alcohol (PVA) is excellent physical properties, biodegradable properties, chemical resistance, hydrophilic and good mechanical properties in the dry state. Thus, PVA became one of the most popular and suitable polymeric material for electrospinning due; its non-toxicity easiness in water solubility and rather easy

to control the morphology even for composites nano fibrous web<sup>12</sup>. These properties of PVA provide a scope to develop range of PVA nano fibrous based textiles. However, PVA has a poor water resistance leads to easy destroy of nano fibrous web structure upon treating with water and hence fibrous web structure limits its applications. Considering these facts it is necessary to enhance the mechanical and wet ability properties of PVA electrospun nano fiber web to widen its application in the area of defence nano based textiles such as clothing for glacier, ballistic and NBC scenario; camouflage fabrics; tents, shelters and habitats and; textile based medical category items. The scope of PVA nanofibres based composite (after removal of limitations) will ensure in the development of completely new textile constructions integrated into functional applications for the use in defence clothing. Few examples for future applications of nanofibres in defence textiles, which are relevant; fire protection suits, thermal protection suits, chemical and biological protection, antimicrobial and UV protective clothing<sup>13-14</sup>. Therefore, the new products can be constructed into various forms and structures to meet the needs for a variety of defence applications.

Water-insoluble electrospun PVA membranes are often produced in a two step process: first an aqueous PVA solution is electrospun to generate nanofibrous membranes and then the membranes are crosslinked *ex situ* by exposure to with glyoxal, dialdehyde, diacid and with a non-solvent for PVA such as acetone or ethanol have been examined<sup>15-16</sup>. While it is desirable to eliminate post-electrospinning treatment and accelerate the production process, very limited work has been done in trying to crosslink PVA or other nanofibers in a simple, one step process via latest needleless nanospider technique. To obtain uniform electro spun coated web via *in-situ* process on such needleless technique is itself a challenging task in terms of controlling the process parameters. .

In this study, PVA nanofibrous web is prepared and coated on Polypropylene non woven fabric by needleless electrospinning technique in one step process. An attempt has been made to; establish *in-situ* electro spinning coating process and determine the properties. Field emission Scanning Electron Micrograph (FESEM), Fourier Transform Infrared (FTIR) spectrometry, DSC analysis, mechanical and absorbency properties were employed to characterize the morphology, thermal and structural behavior of crosslinked and non crosslinked PVA nano fibrous web. In this work, the differences of morphology and chemical structure between the non crosslinked and crosslinked nano fibrous webs were highlighted. The result shows that the nano fibrous web gets flattened and new crystalline morphology has been developed after crosslinking. The transitions from uniform fibers to flattened fibers indicate increased molecular chain entanglement due to the presence of crosslinking agent.

## EXPERIMENTAL

### Materials

In this work, hydrolyzed (87-89%) PVA grade from Aldrich Company was dissolved by magnetic stirring at 80 °C in distilled water for 3 hours. Dicarboxylic acid based commercially available cross linking additive is mixed in PVA solution mainly in three different concentrations; 1%, 2 % and 3 % (% w/v).

### Process Details

In the present study, prepared PVA solution and PVA solution with crosslink (*in-situ*) was electrospun through needleless techniques under identical optimized electro spinning process parameters. PVA solution and PVA solution with crosslinked (*in-situ*) was loaded into a spinning electrode and subjected to applied voltage of 65 kV. Spinning electrode was rotated at 8 rpm. The distance between the spinning electrode and collecting electrode is positioned between 150 mm. A rotating drum is dipped into a bath of liquid polymer. The thin layer of polymer is carried on the spinning drum surface and exposed to a high voltage electric field and subsequently nano fibrous web layer coated on non woven polypropylene

non-woven fabric. Obtained nano fibrous web samples were air dried for 20 minutes to remove residual water molecules if any. Fabricated web with 3 % crosslinking agent was cured at 145 °C for 1 minute in order to observe and compare the combined effects of crosslinking and temperature.

### Surface Morphology Characterization

The surface morphology of PVA electrospun neat PVA nano fibrous web and crosslinked samples were examined by using of field emission scanning electron microscopy (Zeiss).

### Chemical Analysis

Fourier transform infrared spectroscopy (FT-IR) spectra of web were recorded in a Perkin Elmer FTIR instrument (model Perkin Elmer Spectrum 100) from HATR unit. The spectra over the range 4000-650  $\text{cm}^{-1}$  are obtained at a resolution of 4  $\text{cm}^{-1}$ .

### Thermal Analysis

In order to observed the effects of crosslinking agent on thermal properties, differential scanning calorimetry analysis was done for cross linked and non cross linked PVA webs. Differential scanning calorimetry (DSC) was carried out using a TA instruments Ltd DSC 2920 V2. 6A. 6-10 mg of the sample was cut from the test specimen and the measurements were made in aluminum sample pans, over the range 25-250°C, with a heating rate of 10 °C  $\text{min}^{-1}$  and with flowing nitrogen as purge gas

### Resistance to Water-Penetration by Drop Absorbency Test

Nano fibrous web membrane was placed under the burette and a single drop of water was subjected to web through burette as per AATCC Test Method 79 for absorbency <sup>17</sup>. Time of absorbency was measured by stop watch. The five readings were noted at different places of web and mean of the same is recorded.

### Mechanical Characterization

The tensile properties (tensile stress and % elongation at break) of the fibrous web were measured on universal tensile testing machine at a crosshead speed of 10 mm/min with a specified sample size (length = 20 mm & width = 10 mm). In order to prevent the grips from direct contact with the fibrous web, cushion double sides sticky paper tape were used. Five random samples were tested and mean values are reported. The detailed of procedure is described elsewhere <sup>18</sup>.

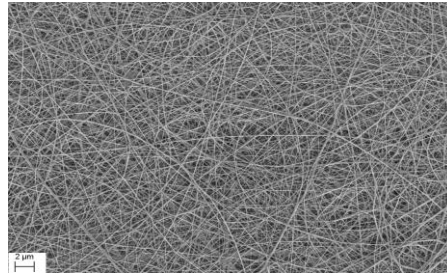
### Surface Profilemetry

The topography (roughness) of the nanofibrous samples are measured by  $\mu\text{Scan}$  (Nano Focus Inc.) using a confocal sensor of crosslinked and non crosslinked PVA web samples.

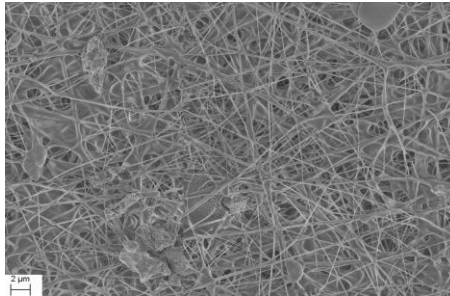
## RESULTS AND DISCUSSIONS

### Surface Morphology

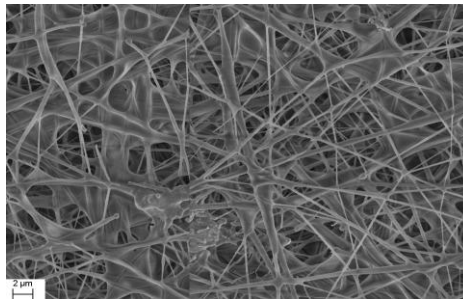
Figure 1 (a , b, c , d & e ) is FESEM microphotographs of PVA spun nano fibrous web with varying concentration of cross linking agent ; a- 0%, b -1% , c -2% , d- 3 % and e - 3% crosslinked- cured respectively.



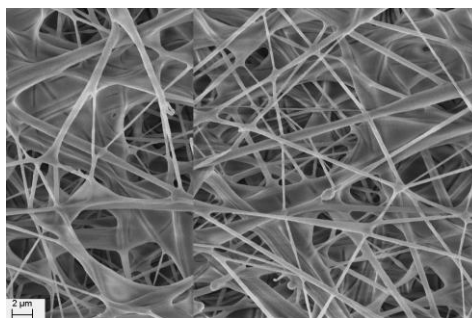
(a)



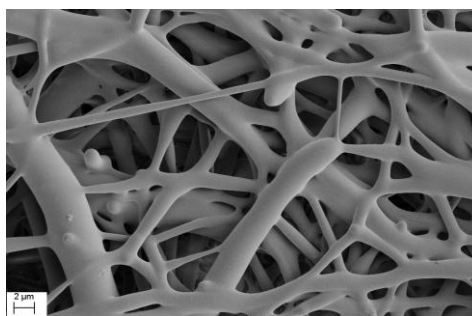
(b)



(c)



(d)



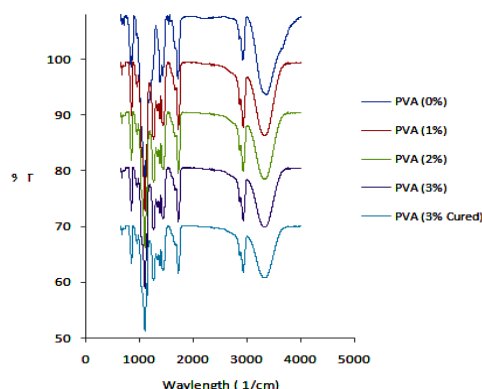
(e)

**Figure 1: Structure Comparison Among Crosslinked and Non Crosslinked as Depicted by FESEM Photographs of PVA Nano Fibrous Web of Varying Concentration ; a- 0%, b-1%, c- 2% d-3% and e-3% -Cured Respectively**

The crosslinked fibers web appeared relatively flattened fibrous structure (Figures b-e) as compared to non crosslinked sample Figures 2(a). An increasing trend (qualitatively) of flattened of fibrous web structure was also observed with respect to concentration of crosslinking agent in PVA solution. This signifies that higher the cross linker concentration more will be the cross linking reactions and thereby more flattened of fibrous micro structure. This flattened micro structure of nano web fibers is may be due to formation of new crosslinking bonds, which tends to squeeze the fibrous micro structure. Moreover, cured crosslinked produced a more flattened fibrous network than uncured cross linked PVA (Figure 1 e). Flattened PVA fibers have been previously observed and attributed to crosslinking<sup>15-16</sup>. On curing, crosslinked reaction may be accelerated due to heat treatment and thereby formation of more number of new crosslinking bonds as compared to uncured samples. This is closely associated with the high crosslinking density in cured PVA nanofibers. Porous structure between fibers is still retained (Figures 1 b-e) even after cross linking. Moreover, between fibers porosity is not affected by flattening of fibrous web.

### Chemical Analysis

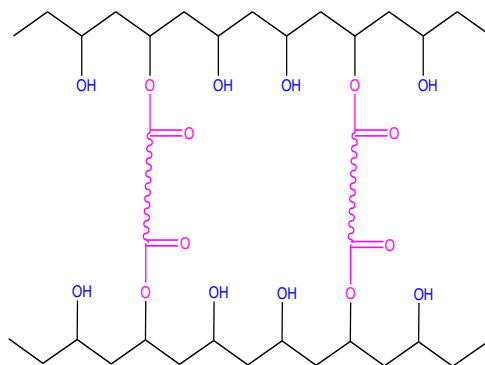
Fourier transform infrared spectroscopy (FITR) was used to monitor the effects of crosslinking agent on chemical structure of PVA electro spun fibrous web. A FITR spectrum of PVA non crosslinked and crosslinked nano fibrous web is shown in Figure 2.



**Figure 2: FTIR Spectra of PVA Nano Fibrous Web**

In PVA non crosslinked and crosslinked web, the peak at  $3334\text{ cm}^{-1}$  show the presence of hydroxyl group. The peak at  $2922\text{ cm}^{-1}$  &  $2852\text{ cm}^{-1}$  is due to C-H stretching vibration which confirms the presence of aliphatic C-H bond in PVA non crosslinked and cross linked sample. Peak at  $1096\text{ cm}^{-1}$  is because of C-O stretching vibration in PVA. In crosslinked sample, peak at around  $1258\text{ cm}^{-1}$  is due to C-O stretching vibration of ester linkage and thereby confirmed formation ester product. No such stretching peak is observed in case of non crosslinked sample. Figure 2, it is clear that there is decrease in number of hydroxyl group in polymer. A decrease in intensity ratio  $I_{\text{OH}} / I_{\text{CH}}$  peak confirms, the cross-linking reaction has taken place in crosslinked PVA samples. It is also seen that on increasing concentration of crosslinker, there was further decrease in intensity ratio  $I_{\text{OH}} / I_{\text{CH}}$  peak. Moreover, on increasing concentration of crosslinker, there will be more consumption of crosslinker and hydroxyl group of PVA during crosslinking reactions, accordingly more number of hydroxyl groups is decreased and which is resulted and reflected into further decrease in intensity ratio  $I_{\text{OH}} / I_{\text{CH}}$  peak as evident from Figure 2. The same trend of FTIR graph is observed for crosslinked- cured PVA sample, where highest decrease in intensity peak ratio  $I_{\text{OH}} / I_{\text{CH}}$  was found. This may be due to cure, crosslinked reaction is accelerated in comparison to uncured crosslinked 3% PVA samples. However, limited information for crosslinking agent as a dicarboxylic acid type was only available. Moreover without detailed knowledge of the exact structure of the cross linking agent, it is difficult to speculate exact chemical reaction involved in crosslinking PVA.

The proposed structure and how chemically this polymeric cross linker is crosslinked to PVA nanoweb are shown in the Figure 3

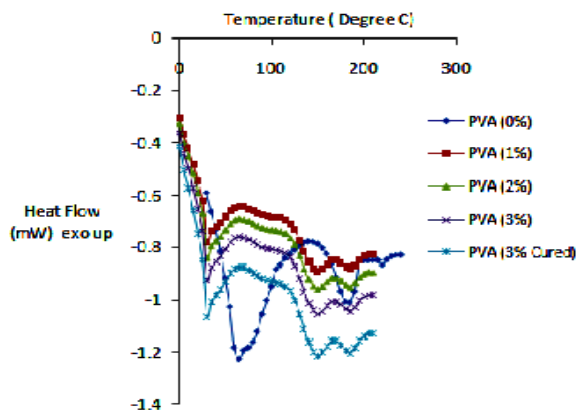


**Figure 3: Proposed Cross-Linked Reactions & Network Structure with PVA**

It has a functional carboxyl group in every monomer unit to react with PVA. Strong cross-linking by ester linkage is formed between the hydroxyl group of PVA and the carboxyl group of dicarboxylic acid to form ester linkage. Such formation of ester compound is also revealed by FTIR analysis Figure 2

#### Thermal Analysis

Figure 4 presents the DSC thermographs over the temperature range 50-250 °C for crosslinked (3%) and non crosslinked PVA electrospun nano fibrous web respectively.



**Figure 4: DSC Thermographs of PVA Non Crosslinked and Crosslinked Web Samples**

As shown in Figure 4, there is one obvious endothermic peak in curves at around 35 °C and 65 °C for crosslinked and non cross linked web samples respectively, which may be related to the moisture of the samples. The second endothermic melting peaks appear around 180 °C of PVA non crosslinked webs. It can be seen from Figure 4 that cross linked webs melting peak (150-185 °C) is resolved into two peaks. However, this peak resolution is more visible in the case of cross linked PVA webs. There is a no such peak resolution for the non crosslinked PVA samples. However resolution of peak is more pronounced with increasing cross linking %. Thus a new melting peak at 150 °C in cross linked PVA is a result of decrease in PVA chain mobility due to the chemical cross-links. This DSC results suggests the formation of new crystalline morphology giving rise to a different melting endotherm upon crosslinking reaction.

#### Mechanical and Hydrophilicity Analysis of Webs

Table 1 presents the mechanical properties and time of absorbency (hydrophilicity) of non crosslinked PVA and crosslinked samples.



**Table 1: Mechanical Properties and Absorbency of PVA Nano Fibrous Web**

Samples	Time of Absorbency Mean Values (sec.)	Mean Tensile Stress ( MPa)	% Elongation at Break
PVA	30	6.7	97.2
PVA 1%	140	8.9	130.1
PVA 2%	190	3.1	45.4
PVA 3%	210	2.2	23.1
PVA 3%- cured	510	1.6	16.5

\* % indicates the concentrations of cross linking agent in PVA

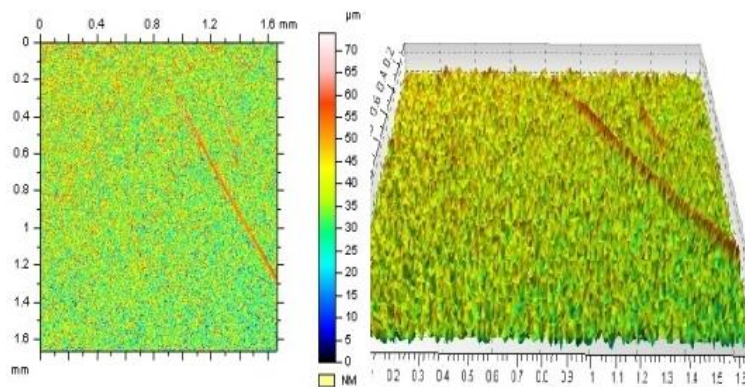
From Table 1, a decreasing trend of mechanical properties with respect to concentration is observed from 2% concentration of crosslinking agent. However there is an increase in strength and % elongation was found in web having 1% concentration of crosslinker. It is also found that heat treated crosslink-cured samples have lower strength and % elongation at break as compared to all other PVA crosslinked samples.

Hence thermal treatment is also playing vital role in extent (degree) of cross linking reactions in PVA. These results suggest that crosslinked PVA nanofibers are higher cross-linking density protects the fiber to elongate, and it became stiffer, thus there is decrease in breaking strength and elongation at break. This is possibly, attributable to flexibility of PVA molecular chain and to the higher crosslinking density in the PVA nanofibers which is restricting the mobility of chains which is impacted on elongation of webs and tensile properties.

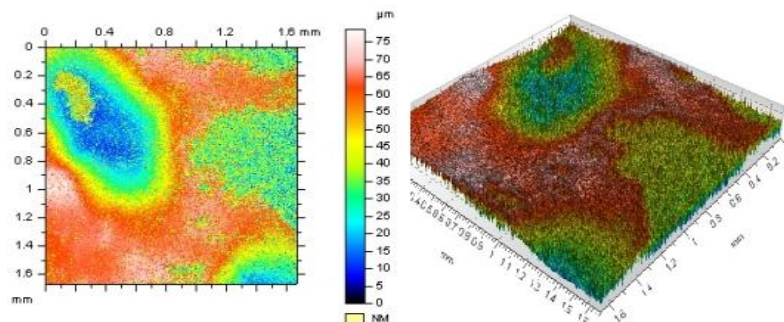
This finding is well supported and in close agreement with the results of FTIR analysis as shown in Figure 2. The increasing trend of absorbency with concentrations of crosslinker is observed. Hence cross linked- cured web samples have the highest water protection than all other samples crosslinked samples. This signifies that crosslinked samples having –OH hydrophilic polar groups (water absorbent group) reacted with crosslinking agent as shown in Figure 3 to form ester linkage. Therefore there is decrease in –OH hydrophilic groups, which is resulted in enhanced protection of cross linked and crosslinked -cured web from water<sup>16,19</sup>.

### Topography (Roughness) of the Nanofibrous

Basically crosslinking is one of the chemical which affects the surface roughness of nano-fibrous web preparation. Figure 5 ( a & b) is the 3-D measuring plots of the nano-fibrous webs are shown, in which light (maximum) and dark (minimum) colors indicate the variation in topography of non crosslinked and 3 % crosslinked PVA web samples respectively.



(a)



(b)

**Figure 5: a & b Surface Profilemetry of PVA Nano Fibrous Web Surface (a) Non Crosslinked and (b) Crosslinked**

Root mean square (RMS) deviation of the roughness profile are respectively 5.56 and 25.25 in wavelength bands ( $\mu\text{m}$ ) for non crosslinked and crosslinked webs respectively. Hence, it is confirmed that in-situ electrosinng with crosslinking makes much impact on the surface roughness of these spun nano-fibrous webs. The rough surface (wavy surface) properties could be exploited as an additional feature. Such wavy surface properties will be facilitated lesser extent of water to penetrate inside the web. Thereby, enhanced water protection properties could be utilized by roughened surface.

## CONCLUSIONS

In this study, we undertake a systematic approach to develop and examine an in-situ process to electrospun crosslinked nanofibers wherein nano-fibrous web is coated ( $0.1 - 2 \text{ g/m}^2$  add on) on Polypropylene (PP) non woven fabric and succeed in determination of nano fiber properties. The chemical structure of the PVA nanofiber web was changed by reaction of dicarboxylic acid with hydroxyl groups of PVA via esterification reactions. The crosslinking reaction causes significant changes in fiber morphology and surface smoothness of web. An addition of crosslinker, confirmed that web still retain the porous (between fibers) morphological structure. Formation of new crystalline morphology upon crosslinking of PVA is also revealed. However, PVA nano fibrous web structure could be destroyed by drop of water. We have demonstrated that in-situ techniques of electro spinning showed better protection of PVA web from water. Cured – crosslinked webs showed high degree of crosslinking effects in terms of morphological and structural changes. The coated Nano-fibrous membranes are highly porous (between fiber) and flattened structure with excellent pore interconnectivity. These webs coated on Polypropylene fabrics could possibly further be exploited for development of futuristic nano-fibrous light weight NBC (nuclear, biological and chemical) protective defence applications. Therefore, this study provided not only the understanding of in-situ crosslinking needleless electro spinning techniques but also showed how web could be exploited in useable textile. Furthermore study could be extended to observe the functional properties; such as growth and filtration of fungi, bacteria and viruses by crosslinked webs.

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